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ORGANOPHOSPHORUS ESTERS—I*

t-BUTYL AS PROTECTING GROUP IN PHOSPHORYLATION VIA NUCLEOPHILIC DISPLACEMENT

A. Zwierzak and M. Kluba

Institute of Organic Chemistry, Technical University (Politechnika), Lodz 40, Poland

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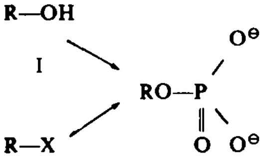
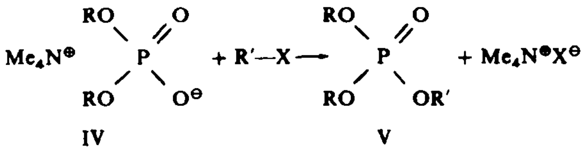
Abstract—Tetramethylammonium di-t-butyl phosphate (VI), readily prepared from di-t-butyl phosphite in good yield, was found to be a convenient phosphorylating reagent for organic halides. In boiling dimethoxyethane it reacts easily, especially with bromides and iodides, to form the corresponding alkyl di-t-butyl phosphates (XI). The phosphotriesters (XI) were converted into the corresponding monoalkyl phosphates (XII) by treatment with trifluoroacetic acid in benzene at room temperature. The products were easily isolated and characterized as anilinium salts (XIII).

Methods for the synthesis of phosphoric acid esters have been the subject of numerous investigations and several phosphorylating agents have been so far introduced. Although various chemical methods for the conversion of an alcohol (I) into the corresponding monophosphate ester (II) have been known for a long time,[1] there appears to be no recorded example of simple and convenient phosphorylation of organic halides (III).



III II

Sodium and potassium dialkyl phosphates have been recognized for a long time as very poor nucleophiles[2] and their displacement reactions with organic halides were not reported to be of any preparative importance. Recent successful application of tetramethylammonium dialkyl phosphates (IV) for the synthesis of mixed phosphotriesters (V) by the group of French investigators[3] called our attention to this reaction as a potential phosphorylating procedure.



$$Me_4N^{\oplus}\,(RO)_2P(O)O^{\ominus} + R'{-}X \rightarrow (RO)_2P(O)OR' + Me_4N^{\oplus}X^{\ominus}$$

IV V

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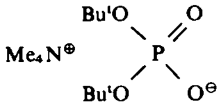
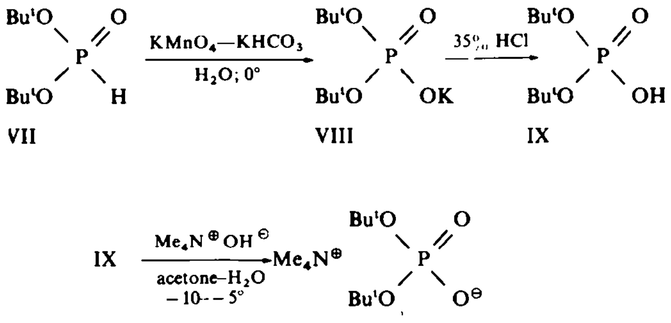
* Paper CLV on organophosphorus compounds.

An important consideration in the use of a method of phosphorylation, clearly, is the ease and selectivity with which both of the protecting groups (in our case R) may be removed from the initial products of phosphorylation (V). It was hoped that t-butyl groups would fulfil this criterion. With this idea in mind we have devised tetramethylammonium di-t-butyl phosphate (VI) as a monofunctional reagent of choice, which, as we shall attempt to show here, appears to be a useful phosphorylating agent for organic halides.



VI

Tetramethylammonium di-t-butyl phosphate (VI) may be obtained in excellent yield by the following reaction sequence:



VII VIII IX

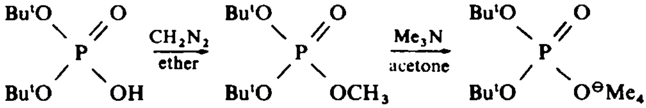
VI

Oxidation of di-t-butyl phosphite (VII) by means of potassium permanganate occurs in alkaline aqueous solution ($KHCO_3$) according to the previously described procedure.[4] The resulting potassium di-t-butyl phosphate (VIII) is perfectly stable at ambient temperature and can be stored indefinitely as dry solid or in aqueous solution. It can be converted into the free acid (IX) in virtually quantitative yield by acidifying the solution with a slight excess of concentrated hydrochloric acid. Di-t-butyl phosphate (IX) is a white, crystalline solid (m.p. 83–84°), sparingly soluble in cold water and very easily soluble in all typical organic solvents. It undergoes spontaneous autocatalytic decomposition into isobutylene (partially into di- and tri-isobutylenes) and phosphoric acid when kept at room temperature for several hours, but it remains unchanged when refrigerated at $-15°$ for indefinite periods of time. In contrast to the free acid (IX) its salts with amines are very stable crystalline solids and can be recommended as convenient derivatives of (IX).

Preparation of tetramethylammonium di-t-butyl phosphate (VI) can be readily accomplished by careful neutralization of tetramethylammonium hydroxide with di-t-butyl phosphate (IX) in water-acetone solution. The reaction should be carried out at low temperature (-10 – $-5°$) with efficient stirring and cooling, the pH value of the resulting solution being adjusted at *ca* 7–7·5. The solution should be evaporated in vacuo at slightly elevated temperature (30–40°) and the crystalline residue dried over phosphorus pentoxide. All these precautions are extremely important in order to avoid the formation of undesirable by-products due to partial dealkylation of particularly acid-labile t-butyl groups.

Nevertheless tetramethylammonium di-t-butyl phosphate (VI) is easy to prepare on a molar scale (Experimental) and is a stable cystalline compound (m.p. 224·5–225° dec.) which, although very hygroscopic, may be kept indefinitely in a sealed vessel.

Alternative procedure leading to (VI) was based on esterification of di-t-butyl phosphate (IX) by means of diazomethane to give methyl di-t-butyl phosphate (X).



IX X VI

The latter would then be expected to undergo demethylation in boiling acetone solution of trimethylamine to give directly the desired tetramethylammonium salt (VI). Contrary to the expectations the phosphotriester (X) was not attacked by trimethylamine, possibly for steric reasons.

Neither potassium nor cyclohexylammonium di-t-butyl phosphate were found to react with organic halides in boiling dimethoxyethane to any appreciable extent. This pronounced lack of reactivity can be tentatively attributed to the presence of strongly H-bonded or mostly unionized species in solution which markedly reduces the nucleophilicity of di-t-butyl phosphate anions. In contrast to this, tetramethylammonium di-t-butyl phosphate (VI) readily reacts, as expected, with primary and secondary organic halides. In this particular case the enhanced nucleophilic reactivity of di-t-butyl phosphate anions is evidently due to the presence of free, unsolvated species in the solutions of VI in typical dipolar aprotic solvents, like nitromethane, acetone or dimethoxyethane. The latter was found to be the solvent of choice. Good yields of the phosphotriesters (XI) are obtained on refluxing stoicheiometric amounts* of the corresponding halide and phosphorylating agent (VI) in dimethoxyethane. This reaction and the following processes leading from the halide molecule to the corresponding phosphorylation product—anilinium monoalkyl phosphate (XIII) are outlined on the scheme.

It is not necessary or desirable to isolate the intermediate phosphotriesters (XI). If the phosphorylation products are treated with at least one molecular equivalent of trifluoroacetic acid† and then with an excess of aniline, the phosphotriesters (XI) are quantitatively converted into the corresponding monophosphate esters (XII) isolated and characterized as stable, crystalline anilinium salts (XIII).

The yields of products, which are good with respect to both the halide and the phosphorylating agent, together with the elemental analysis data are listed in Table 1. The

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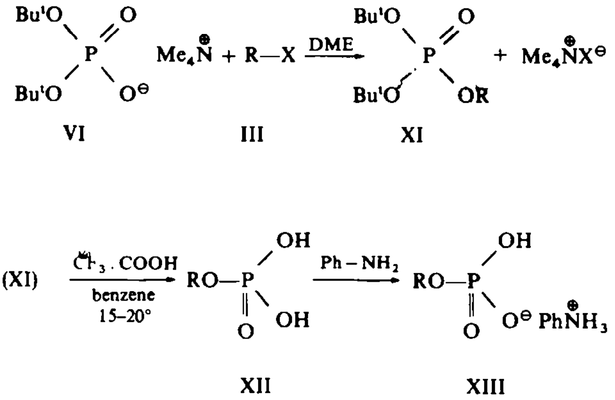
* Slight excess (10%) of the halide was used in the case of low boiling compounds.

† Dry hydrogen chloride in chloroform at room temperature can also be employed for removal of t-butyl groups, but an excess of HCl must be thoroughly expelled from the reaction mixture before adding aniline. Thus trifluoroacetic acid seems to be the preferred dealkylating agent.

SCHEME



structure of all anilinium monoalkyl phosphates was confirmed by IR and NMR spectroscopy. The relevant data are compiled in Table 2.

The influence of the leaving group on the overall yield of phosphorylation was tested, n-butyl halides (Bu^nX, X = Cl, Br, I) being used as model compounds. No considerable difference was observed in the case of bromides and iodides—yields of 68·5% and 65% of the corresponding anilinium salt (XIII, R = Bu^n) were obtained respectively under comparable conditions. n-Butyl chloride was distinctly less reactive than bromide and iodide affording anilinium-n-butyl phosphate (XIII, R = Bu^n) in 12% yield only. In general lower yields of (XIII) were also obtained when secondary alkyl halides were employed as starting materials (Table 1, compounds 4 and 7). Cyclohexyl bromide, possibly due to steric retardation, was found to be completely unreactive towards (VI) in boiling dimethoxyethane.

TABLE 1. ANILINIUM MONOALKYL PHOSPHATES $(RO)(HO)P(O)O^{\ominus}\ Ph\overset{\oplus}{N}H_3$

Compound No.	Alkyl halide	Yield %	M.p°C	M.p.°C (Literature data[6])	Analyses (%) Required C	H	P	N	Found C	H	P	N
1	CH_3I	95	162–5	167–8	41·0	5·85	15·1	6·8	41·1	5·9	14·9	6·8
2	C_2H_5Br	84·5	145–7	164–6	43·9	6·4	14·2	6·4	43·9	6·3	14·5	6·6
3	n—C_3H_7Br	87	135–7	137–9	46·3	6·9	13·3	6·0	46·2	6·7	13·3	6·3
4	i—C_3H_7Br	50·5	166–8	159–60	46·3	6·9	13·3	6·0	46·2	7·1	13·5	6·1
5	n—C_4H_9I	65	138–40	138–40	48·9	7·3	12·5	5·7	48·4	7·2	12·7	5·8
6	i—C_4H_9Br	40·5	155–7	155–6	48·9	7·3	12·5	5·7	48·5	7·15	12·9	5·7
7	sec—C_4H_9Br	36	155–7	—	48·9	7·3	12·5	5·7	48·7	7·3	12·7	5·5
8	$CH_2=CH$—CH_2Br	83	136–8	—	46·7	6·1	13·4	6·1	46·8	6·1	13·2	6·25
9	Ph—CH_2—Cl	61*	158–60	150–3	55·5	5·7	11·0	5·0	55·2	5·7	10·9	4·9

* Benzyl dihydrogen phosphate was obtained as colourless solid in 70·5% yield. M.p. 104·5–105·5° NMR(D_2O): δ, 4·85 (s, O$\underline{H}$); 5·00 (d, C$\underline{H}_2$, J_{P-O-CH_2} = 7·8 Hz). 7·41 (s. $C_6\underline{H}_5$).

TABLE 2. IR AND NMR SPECTRAL ASSIGNMENTS OF ANILINIUM MONOALKYL PHOSPHATES

(RO)(HO)P(O)O$^{\ominus}$ Ph$\overset{\oplus}{N}$H$_3$

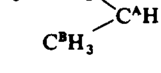
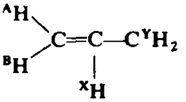
Compound No	R	IR (KBr)[a] cm^{-1}	NMR (D$_2$O with DSS as int. ref.) chemical shifts (δ, ppm; J, Hz)[b]
1	CH$_3$	2560s, 2150m, 1630m [P(O)OH], 1225s, 1020vs [PO$_2^{\ominus}$?], 1500s [NH$_3^{\oplus}$], 1160vs [C—O—(P)], 1050vs, 950vs [P—O—(C)], 740s [arom]	δ = 3·58 (d, 3H, J_{P-O-CH_3} = 10·8), 4·93 (s, NH$_3^{\oplus}$, OH), 7·43 (m, 5H, arom)
2	C^{B}H$_3$—C^{A}H$_2$	2580s, 2150m, 1640m [P(O)OH], 1218s, 1030s [PO$_2^{\ominus}$?], 1500s [NH$_3^{\oplus}$], 1150s [C—O—(P)], 1060vs, 962vs [P—O—(C)], 740s [arom]	δ = 1·23 (t, 3H$_B$, $J_{H_A-H_B}$ = 7·1), 3·88 (q, 2H$_A$, J_{P-O-CH_2} = $J_{H_A-H_B}$ = 7·1), 4·79 (s, $^{\oplus}$NH$_3$, OH). 7·38 (m, 5H, arom)
3	C^{C}H$_3$—C^{B}H$_2$—C^{A}H$_2$	2560s, 2120m, 1630m [P(O)OH], 1210s, 1030s [PO$_2^{\ominus}$?], 1495s [NH$_3^{\oplus}$], 1140s [C—O—(P)], 1000s, 950s [P—O—(C)], 740s [arom]	δ = 0·92 (t, 3H$_C$, $J_{H_B-H_C}$ = 7·1), 1·55 (m, 2H$_B$), 3·80 (qt, 2H$_A$, $J_{H_A-H_B} \simeq J_{P-O-CH_2} \simeq$ 6·5), 4·93 (s, NH$_3^{\oplus}$, OH), 7·45 (m, 5H, arom)
4	(C^{B}H$_3$)$_2$C^{A}H	2550s, 2140m, 1620m, [P(O)OH], 1215s, 1030vs [PO$_2^{\ominus}$?], 1495s NH$_3^{\oplus}$], 1120vs, 1140vs, 1165s [C—O—(P)], 1010s, 958vs [P—O—(C)], 740s [arom]	δ = 1·25 (d, 6H$_B$, $J_{H_A-H_B}$ = 6·0), 4·38 (m, 1H$_A$), 4·83 (s, NH$_3^{\oplus}$, OH), 7·42 (m, 5H, arom)
5	C^{D}H$_3$—C^{C}H$_2$—C^{B}H$_2$——C^{A}H$_2$	2560s, 2130m, 1630m [P(O)OH], 1215s, 1030vs [PO$_2^{\ominus}$?], 1495s [NH$_3^{\oplus}$], 1150s [C—O—(P)], 950vs [P—O—(C)], 740s [arom]	δ = 0·90 (distorted t, 3H$_D$), 1·05–1·80 (m, 4H$_{B,C}$), 3·80 (qt, 2H$_A$, $J_{H_A-H_B} \simeq J_{P-O-CH_2} \simeq$ 6·0), 4·76 (s, NH$_3^{\oplus}$, OH), 7·39 (m, 5H, arom)
6	(C^{C}H$_3$)$_2$C^{B}H—C^{A}H$_2$	2570s, 2120m, 1640m [P(O)OH], 1220s, 1030vs [PO$_2^{\ominus}$?], 1500s [NH$_3^{\oplus}$], 1150s [C—O—(P)], 950vs [P—O—(C)], 742s [arom]	δ = 0·90 (d, 6H$_C$, $J_{H_B-H_C}$ = 6·5), 1·78 (m, 1H$_B$), 3·58 (t, 2H$_A$, $J_{H_A-H_B}$ = $J_{P-O-CH_2} \simeq$ 6·4), 4·80 (s, NH$_3^{\oplus}$, OH), 7·42 (m, 5H, arom)
7		2600s, 2170m, 1610m [P(O)OH], 1230s, 1020s [PO$_2^{\ominus}$?], 1500s [NH$_3^{\oplus}$], 1140s [C—O—(P)], 1000s, 980vs, 965vs [P—O—(C)], 740s [arom]	δ = 0·90 (distorted t, 3H$_D$ $J_{H_C-H_D}$ = 7 7) 1 24 (d, 3H$_B$, $J_{H_A-H_B}$ = 6 45), 1·59 (m, 2H$_C$). 4·16 (m, 1H$_A$), 4·83 (s, NH$_3^{\oplus}$, OH), 7·45 (m, 5H, arom)
8		2570s, 2150m, 1630m [P(O)OH], 1215s, 1030vs [PO$_2^{\ominus}$?], 1498s [NH$_3^{\oplus}$], 1150s [C—O—(P)], 950vs [P—O—(C)], 745s [arom]	ABXY$_2$ system[c]: δ_Y = 4·31 (12 lines, 2H$_Y$), δ_A = 5·28, δ_B = 5·16 (AB part, 8 lines, 2H$_{AB}$) δ_X = 5·97 (12 lines, 1H$_X$); J_{AX} = 17·4, J_{BX} = 10·0, J_{AB} = 2·1, $J_{Y(AB)}$ = 1·3, J_{XY} = 4·8, J_{CH_Y-O-P} = 7·5; δ = 4·89 (s, NH$_3^{\oplus}$, OH), δ = 7·40 (m, 5H, arom)

TABLE 2—contd.

Compound No	R	IR (KBr)[a] cm^{-1}	NMR (D_2O with DSS as int. ref.) chemical shifts (δ, ppm; J, Hz)[b]
9	Ph—CH_2	2560s, 2290m, 1620m, [P(O)OH], 1220s, 1030vs [$PO_2^{\ominus}$?], 1495s [$NH_3^{\oplus}$], 1145s [C—O—(P)], 1050vs, 960vs [P—O—(C)], 735s [arom]	δ = 4·74 (s, $NH_3^{\oplus}$, OH), 4·85 (d, 2H, $J_{CH_2-O-P} \simeq 6{\cdot}7$), 7·36 (m, 5H, arom)

[a] Only characteristic absorption bands are included.

[b] Abbreviations used: s, singlet; d, doublet; t, triplet; qt, quartet;, q, quintet; m, multiplet.

[c] First order treatment was applied.

Experimental evidence presented in Table 1 points evidently to the preparative usefulness of the devised phosphorylation procedure. The method appears to be particularly suited to the phosphorylation of polyfunctional organic halides containing no acid-labile groups. Further investigations on this subject are now in progress.

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. Dimethoxyethane was dried over NaH. Light petroleum refers to the fraction boiling at 60–80°. All extracts were dried over $MgSO_4$ and evaporated under reduced press. B.ps and m.ps (taken in capillaries) are uncorrected. NMR spectra were measured at 60 MHz with a Jeol JNM-C-60 HL spectrometer in $CDCl_3$ or D_2O solns using TMS or DSS as internal standards, respectively. IR spectra were recorded using a Spectromom 2000 spectrophotometer (MOM, Budapest). Measurements were made on samples of analytical purity.

Tetramethylammonium iodide. MeI (71·0 g, 0·5 mole) was added to a soln of Et_3N (23·6 g, 0·4 mole) in acetone (150 ml) at 10–20° with stirring and occasional cooling. After 1 hr at 15–20° the mixture was cooled to 0° and precipitated tetramethylammonium iodide was filtered off and washed with ice-cold acetone (100 ml); yield—65·7 g (85%).

Tetramethylammonium hydroxide. Freshly prepared suspension of Ag_2O (0·24 mole) in water (100 ml) was added in small portions to a stirred soln of tetramethylammonium iodide (40·2 g, 0·2 mole) in water (300 ml) at 50°. After the addition was complete stirring was continued for 1 hr at room temp. AgI was then filtered off and washed with water (2 × 50 ml). The aqueous soln (*ca* 3%) of tetramethylammonium hydroxide was standardized against 0·1 N HCl in presence of bromothymol blue.

Di-t-butyl phosphite (VII) was obtained in 80–85% yield according to Goldwhite and Saunders.[5]

Potassium di-t-butyl phosphate (VIII). To 38·8 g (0·2 mole) of VII and 12·2 g (0·12 mole) $KHCO_3$ in 170 ml water, finely powdered $KMnO_4$ (23·1 g, 0·14 mole) was added portionwise for about 1 hr under stirring and efficient cooling (ice-salt bath). The temp of the strongly exothermic reaction was kept at 0°. After the addition was complete stirring was continued for 30 min at room temp. The mixture was then heated for 15 min at 60° to coagulate a colloidal suspension of MnO_2, filtered, and the soln decolourized by boiling with charcoal (3 g). Evaporation of the filtered soln afforded VIII as colourless crystalline mass, yield—47·1 g (95%). (Found: P, 12·4; $C_8H_{18}O_4PK$ requires: P, 12·5%). The potassium salt (VIII) can be maintained indefinitely at room temp in aqueous soln of known concentration and used in this form for the preparation of IX.

Di-t-butyl phosphate (IX). Conc HCl (35 ml) was added slowly to the soln of VIII (49·6 g, 0·2 mole) in water (*ca* 250 ml) with stirring and external cooling at 0·5°. Precipitation of IX commenced at once. The colourless, crystalline ppt was filtered off, washed with a small amount of ice-cold water, and dried *in vacuo* over P_2O_5, yield 40·0 g (95%). Crude di-t-butyl phosphate, m.p. 83–84°, was analytically pure. It could be kept at room temp for at most 24 hr without appreciable signs of decomposition. However, on refrigeration to −15°, di-t-butyl phosphate could be stored safely for indefinite periods. (Found: C, 45·8; H, 9·2; P, 14·5;

$C_8H_{19}O_4P$ requires: C, 45·7; H, 9·05; P, 14·8%). The IR spectrum (CCl_4) showed characteristic bands at: 2591m, 2365m, 1670m, br [P(O)OH], 1385m, 1361s (Bu^t), 1230vs (P=O), 1163vs [C—O—(P)], 1031vs, br [P—O—(C)] cm^{-1}. The NMR spectrum (in CCl_4 with TMS as internal reference) showed signals at: δ = 1·45 ppm (s, 9H, CH_3), and δ = 12·50 ppm (s, 1H, O$\underline{H}$).

Anilinium di-t-butyl phosphate. A soln of aniline (2·33 g, 0·025 mole) in light petroleum (10 ml) was added to a soln of di-t-butyl phosphate (5·26 g, 0·025 mole) in the same solvent (30 ml). The crystalline ppt (6·7 g, 88%) was filtered off and washed with light petroleum (2 × 50 ml). The crude salt melted at 110–112°. Crystallization from acetone–light petroleum (1 :10) did not raise the m.p. (Found: C, 55·2; H, 8·7; N, 4·5; $C_{14}H_{26}O_4NP$ requires: C, 55·4; H, 8·6; N, 4·6%).

Cyclohexylammonium di-t-butyl phosphate was prepared in 96% yield as described for the anilinium salt The crude salt melted at 185–186° (dec) and was analytically pure. It crystallized from MeOH acetone (1 :10) in thin, colourless needles, m.p. 185–186° (dec) (Found: C, 54·1; H, 10·4; N, 4·4; $C_{14}H_{32}O_4NP$ requires: C, 54·3; H, 10·4; N, 4·5%).

Dicyclohexylammonium di-t-butyl phosphate was prepared from di-t-butyl phosphate (0·025 mole) and dicyclohexylamine (0·025 mole) in light petroleum (60 ml). The mixture was set aside overnight at room temp. The crude salt (7·5 g, 76%) was filtered off and crystallized from cyclohexane to give colourless crystals, m.p. 177–179°, (Found: C, 61·4; H, 10·6; N, 3·7; P, 8·0; $C_{20}H_{42}O_4NP$ requires: C, 61·3; H, 10·7; N, 3·6; P, 7·9%).

Tetramethylammonium di-t-butyl phosphate (VI). A soln of moist, freshly prepared IX (from 0·2 mole of VIII) in acetone (500 ml) was placed in a 2 l. 3-necked flask equipped with a stirrer, thermometer and dropping funnel. A *ca* 3% aqueous soln of tetramethylammonium hydroxide (0·19 mole) was added dropwise at −10–−5° with efficient stirring and external cooling (ice-salt bath). After the addition was complete a sample of the resulting soln was neutral or slightly alkaline (pH = 7–7·5). On evaporation at slightly elevated temp (30–40°) a colourless, crystalline residue was obtained, which weighed 53·9 g (95% with respect to the K salt) when dried *in vacuo* over P_2O_5. Recrystallization from dimethoxyethane afforded analytically pure VI as a colourless crystalline, strongly hygroscopic powder, m.p. 224·5–225° (dec) (Found: P, 10·9; N, 5·0; $C_{12}H_{30}NO_4P$ requires: P, 10·9; N, 4·9%). The IR spectrum (KBr) showed characteristic bands at: 1490s (Me_4N^+), 1380s, 1360s (Bu^t), 1207s, 1075vs (PO_2^-?), 965vs [P—O—(C)] cm^{-1}. The NMR spectrum (in D_2O with DSS as internal reference) showed signals at: δ = 1·35 ppm (s, 18H, C—C$\underline{H}_3$), and δ = 3·14 ppm (s, 12H, N—C$\underline{H}_3$). Crude, finely powdered material was successfully employed for all reactions with alkyl halides.

Methyl di-t-butyl phosphate (X). An ethereal soln of diazomethane was added at room temp to the stirred soln of di-t-butyl phosphate (21.0 g, 0·1 mole) in light petroleum (200 ml) until the pale yellow colouration of the soln persisted and the evolution of N_2 ceased. The solvent was then evaporated and the residue distilled *in vacuo* to give methyl di-t-butyl phosphate (19·5 g, 87%) as colourless, mobile liquid, b.p. 51°/0·8 mm (bath temp 80–85°), n_D^{20} – 1·4141. (Found: C, 48·3; H, 9·2; P, 13·7; $C_9H_{21}O_4P$ requires: C, 48·2; H, 9·4; P, 13·8%). The IR spectrum (film) showed characteristic bands at: 1718m (?), 1387s, 1364s (Bu^t), 1259vs (P=O), 1172s [C—O—(P)], 1058vs, 1034vs, 990vs [P—O—(C)], 917m, 835vs, 793vs cm^{-1}. The NMR spectrum (in $CDCl_3$ with TMS as internal reference) showed signals at δ = 1·48 ppm (s, 9H, C—C$\underline{H}_3$) and δ = 3·63 ppm (d, 3H, O—C$\underline{H}_3$, J_{P-O-CH_3} = 11·5 Hz).

Attempted demethylation of methyl di-t-butyl phosphate (X) *with trimethylamine.* Methyl di-t-butyl phosphate (12·2 g, 0·05 mole) was refluxed with an excess of Et_3N (5·9 g, 0·1 mole) in acetone (30 ml) for 3 hr. No ppt was formed on cooling the mixture. Distillation *in vacuo* afforded unreacted X in 95% yield.

Phosphorylation of alkyl halides—General procedure. Alkyl halide (0·02–0·022 mole) was added dropwise with stirring to the soln of tetramethylammonium di-t-butyl phosphate (5·7 g, 0·02 mole) in boiling dimethoxyethane (60 ml). The mixture was then refluxed for 3 hr, cooled, and filtered. The filtrate was evaporated, diluted with light petroleum (40 ml), filtered once more and evaporated again. Benzene (50 ml) and trifluoroacetic acid (2·7 g, 0·024 mole) was added to the residue and the soln was set aside for 18 hr at room temp. Crude monoalkyl phosphate, obtained as a thick oil on evaporation of the soln, was dissolved in anhyd. EtOH (25 ml) and aniline (2·5 ml, 0·024 mole) was added to the soln. Compound XIII precipitated immediately. It was filtered off, washed with small amount of anhyd. EtOH, and crystallized from this solvent. Table 1 shows results and analyses.

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